STABILITY OF HIGH PURITY SILICON CARBIDE AND STOICHIOMETRIC SILICON CARBIDE FIBER COMPOSITES AT HIGH NEUTRON FLUENCES —Y. Katoh, L.L. Snead, K. Ozawa (Oak Ridge National Laboratory), T. Nozawa, H. Tanigawa (Japan Atomic Energy Agency)

OBJECTIVE

The objective of this work was to demonstrate the high neutron fluence stability of both monolithic SiC and the current nuclear grade SiC/SiC composite. Materials have been evaluated under a United States Department of Energy (US DOE) / Japan Atomic Energy Agency (JAEA) collaboration in a range of dose up to ~40 displacement per atom (dpa) in the High Flux Isotope Reactor (HFIR).

SUMMARY

High purity chemically vapor-deposited silicon carbide and near-stoichiometric SiC fiber, chemically vapor-infiltrated SiC matrix composite were evaluated following neutron-irradiation to ~28 dpa at 300 and 650ºC and to ~41 dpa at 800ºC, respectively. The irradiated swelling, thermal conductivity, and elastic modulus indicated no change of these properties at high fluences after the initial saturation. With a statistically meaningful sample population, no change in flexural strength of CVD SiC was observed after 300ºC irradiation. A slight decrease in strength was observed after 650ºC irradiation but was attributed to an experimental artifact; specifically, a reaction between samples and the capsule components. The Hi-Nicalon™ Type-S, CVI SiC composite retained the pre-irradiation strength and the non-linear fracture mode. The electrical resistivity measurement revealed a relatively minor effect of irradiation. Overall, irradiation- insensitivity of the high purity SiC ceramics and composite to neutron irradiation to doses 30-40 dpa at temperatures 300-800ºC was demonstrated.

PROGRESS AND STATUS

Introduction

Monolithic silicon carbide (SiC) has been studied for fuel applications in gas cooled reactors for several decades, and for the past two decades as the base material for SiC fiber-reinforced SiC-matrix (SiC/SiC) composites, a potential high-temperature, low-activation structural material for fusion and fission power applications.[1-4] The primary focus of study for the composite material has been the development of a radiation stable material, given the poor as-irradiated performance of early materials.[5-7] Over the past decade significant progress has been made towards this goal with the development of what is now considered a nuclear grade SiC/SiC composite composed of high purity, near-stoichiometric, and dense fibers and matrix. However, these composite materials, and in fact the monolithic chemically vapor-deposited (CVD) SiC which are a critical element of gas-cooled reactor fuels, have not been demonstrated to retain such fundamental properties as strength and dimensional stability under the high-dose irradiation typical of their application. In fact, vast majority of the irradiation effect data published for CVD SiC are those for dose levels below 10 dpa, with some data suggesting a significant degradation in crystalline CVD SiC for doses exceeding 10 dpa.[8] Similarly, the highest neutron dose so far experienced by high purity, near-stoichiometric SiC/SiC composites is 12.5 dpa, although no significant irradiation-induced property modification other than thermal conductivity decrease has ever been reported for these composites by neutron irradiation.[9]

When SiC is irradiated with energetic neutrons, self defects are produced and accumulate in the matrix until the saturation is reached, typically by a few dpa.[3] At the temperatures of common interest for nuclear applications, self-interstitial atoms (SIA) of both types (C and Si) are sufficiently mobile, while the vacancies and SIA clusters are immobile. Therefore, if SIA's are not able to before recombine with vacancies they will remain in the matrix causing volumetric expansion (swelling) and decreased thermal conductivity. Antisite defects are also believed to build up with dose and tend to saturate in concentration, contributing to the observed irradiation effect phenomena. The mechanisms for the saturation in various irradiation-induced changes are not sufficiently understood but are speculated to be related with the

cascade-resolution and the defect interactions with very high concentrations of various type defects and clusters. [10] In this context, whether such irradiation effect phenomena such as swelling and thermal conductivity decrease truly saturate or undergo further gradual evolutions is a question which has not been answered. [3]

The purpose of this work is to report on an irradiation program whose aim is to demonstrate the high-dose stability of both monolithic SiC and the current nuclear grade SiC/SiC composite. Materials have been evaluated under a United States Department of Energy (US DOE) / Japan Atomic Energy Agency (JAEA) collaboration in a range of dose up to 40 displacement per atom (dpa) in the High Flux Isotope Reactor (HFIR).

Experimental Procedure

The monolithic material examined was CVD SiC produced by Rohm and Haas (presently Dow Chemical). This material is of standard resistivity grade and the manufacturer-claimed chemical purity >99.9995%. The composite material used was chemically vapor-infiltrated SiC (essentially CVD SiC) matrix and reinforced with two-dimensional (2D), 5-harness satin-weave Hi-Nicalon™ Type-S (HNLS) SiC fiber fabric in a 0/90º stacking configuration. The fiber fabrics were coated with a ~20 nm-thick pyrolytic carbon (PyC) and ~100 nm-thick SiC alternating multi-layer coating as the fiber-matrix interphase. Details of the interfacial coating is found elsewhere.[11]

Rectangular flexure beams measuring 50.2 x 6.35 x 2.63 (mm) of these materials were irradiated in HFIR at Oak Ridge National Laboratory (Oak Ridge, Tennessee, USA) using the flux trap fixed rabbit tube facility, where the typical fast neutron flux is ~1 x 10^{19} n/m^2/s. The fluences and irradiation temperatures were 27.8 dpa at 300ºC and 28.2 dpa at 650ºC for the CVD SiC and 40.7 dpa at 800ºC for the HNLS composite. The equivalence of 1 dpa with 1 x 10^{25} n/m^2 (E > 0.1 MeV) was assumed for conversion of neutron fluence into displacement damage level. The irradiation temperature was determined by post-irradiation annealing of room temperature electrical resistivity of dedicated CVD SiC thermometry samples.[12]

The post-irradiation examination (PIE) items included flexural strength, dynamic Young's modulus, mass density, thermal diffusivity, and electrical conductivity. Measurements were performed at room temperature with the exception of electrical conductivity. Dynamic Young's modulus was estimated based on determination of fundamental resonant frequency by impulse excitation and vibration method, per ASTM C1259-08. Mass density and swelling was determined by means of a density gradient column technique for the monolithic material. Swelling of the composite was determined by the apparent density measurement. Thermal diffusivity was measured using a flash diffusivity technique, ASTM E1461-07. Electrical conductivity was measured in a four-probe configuration for the in-plane orientation and in a two-probe configuration for the through-thickness orientation.[13]

Flexural strength of the monolithic material was evaluated by a three-point flexure test using miniature samples laterally machined from the beam samples. The support span and the specimen dimensions were 5 mm and measuring 6.35 x 2.63 x 0.5 mm^3, respectively. The original flexure beam samples have reacted with stainless steel springs, with which they had been irradiated in contact, and heavily damaged on one side and have metal slightly deposited from the holder material on the other side. The rational behind the selection of these small beam specimens was two-fold. First, the relatively large CVD SiC beams irradiated to high dose underwent surface reaction with the holder material (likely a chromium vapor plating from the V-4Cr-4Ti holder) and a chemical reaction with the stainless steel springs which were used to ensure thermal contact between the SiC bar and the vanadium holder. The resulting reaction pits, and some resulting cracking compromised the surface of the sample and the possibility of 4 pt. testing of the larger bar. For this reason the microbeam (lateral slices from the larger beam) technique was developed for these specimens. The second reason for utilizing these small samples was that a large number of samples were achieved from each irradiated bar, and previously irradiated bars could be sliced and retested for comparison.

The composite samples did not experience a severe pitting reaction observed for the CVD SiC bars as molybdenum springs were used. However, vapor residue from the V-4Cr-4Ti holder did occur for the composite. To examine the influence of metallic deposition on strength and to best utilize the very limited number of samples available, the original composite beams were machined into four smaller flexure beams of 24.8 x 6.35 x 1.1 mm^3. Testing the sub-sized beams revealed no significant difference in flexural strength or fracture behavior for samples with and without the deposition, thus the potential effect of metallic vapor deposition was ignored in the analysis.

Results and Discussion

Swelling, thermal conductivity, and Young's modulus

The results of PIE are summarized in Table I along with the irradiation conditions. The swelling values at ~28 dpa for the CVD SiC were determined to be ~1.65% and ~0.97% at 300 and 650ºC, respectively, to a high accuracy using a density gradient column. Swelling of the composite material at ~41 dpa was determined to be ~0.68% at 800ºC with less accuracy as it was deduced through standard dimensional measurement. These values appear to be consistent with the literature data for saturation swelling of high purity SiC, most of which had been taken at the doses of a few dpa.[3] Based on this result, we conclude that the true saturation in swelling of SiC in this temperature range had been achieved at much lower doses.

Table I: Summary of irradiation conditions and unirradiated and irradiated properties. Numbers in parentheses are one standard deviations.

	CVD SiC Rohm&Haas			2D-HNLS/ ML/CVI-SiC	
Irradiation Temperature [ºC]	Unirr.	300	650	Unirr.	800
Fast Fluence [dpa]		27.8	28.2		40.7
Mass Density [g/cm^3]	3.210	3.157	3.179	~2.4	~2.4
Swelling [%]	n/a	1.65 (0.04)	0.97 (0.02)	n/a	0.68 (0.01)
RT Thermal Conductivity [W/m-K]	>~300	9.4 (1.1)	12.7 (0.8)	~9.8	~2.7
Young's Modulus [GPa]	450	407 (11)	426 (3)	212 (10)	210 (8)
Number of Flexural Tests	67	24	21	8	7
Proportional Limit Stress [MPa]	n/a	n/a	n/a	317 (27)	330 (20)
Ultimate Stress [MPa]	514 (98)	506 (177)	429 (153)	444 (34)	461 (48)

n/a: not applicable

The monolithic CVD SiC thermal conductivity values at room temperature were determined to be ~9.4 and ~12.7 W/m-K for irradiation temperatures of 300 and 650ºC, respectively, using the measured thermal diffusivity and mass density values and the specific heat data for pure SiC.[3] The composite thermal conductivity in through-thickness direction was determined to be ~2.7 W/m-K, in the same way, with a significant specimen-to-specimen scatter. These data points again coincide with the typical thermal conductivity values anticipated after a few to 10 dpa irradiation at those temperatures, although it is hard to confirm whether or not saturation is truly achieved due to the typically greater relative error in thermal diffusivity measurement.

Both the swelling and the thermal conductivity values obtained are plotted against fluence in Fig. 1, along with the previous data acquired in the identical experimental equipment and procedures. The trend lines were drawn upon assumptions that the both swelling and reciprocal thermal conductivity build up with the 2/3 power of fluence followed by true saturations. [14] The plots of the present data confirm the above observations. The previously speculated gradual increase in swelling and the gradual decrease in thermal conductivity in the saturation swelling regime appear to be negative or very minor if true.

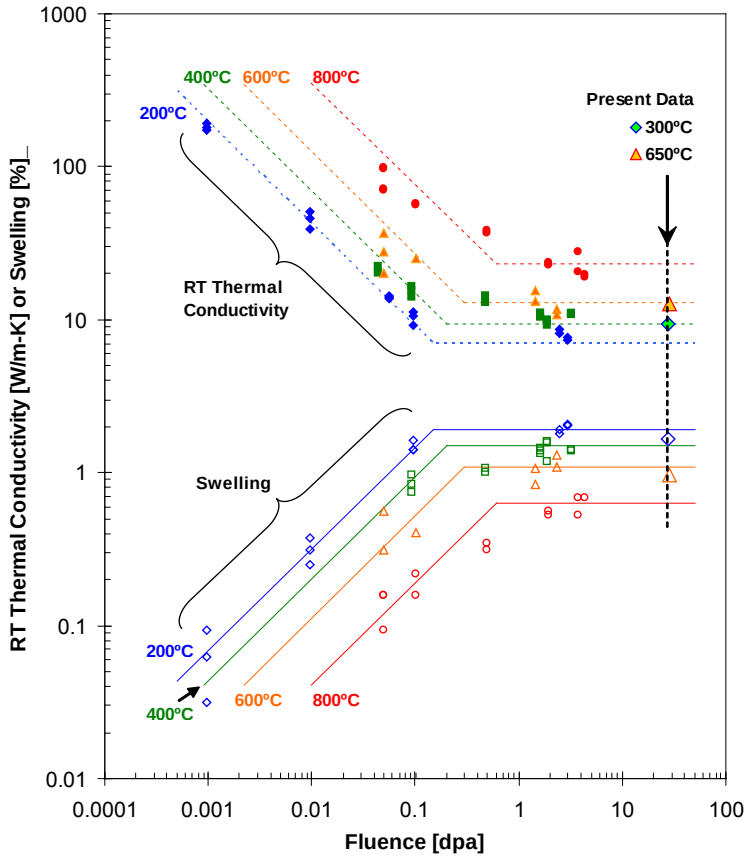

Figure 1: Fluence-dependent evolutions of swelling and thermal conductivity of CVD SiC.

The dynamic Young's modulus exhibited a modest decrease for the irradiated CVD SiC, ~9.5% after 300ºC irradiation and ~5.3% after 650ºC irradiation, and an insignificant change for the composite. The temperature dependency of Young's modulus of the irradiated CVD SiC is consistent with the literature data; however the relative decrease appears to be greater than anticipated from the magnitude of swelling, or approximately three times that of the volumetric swelling.[3] This discrepancy may be reasonably attributed to the lateral cracks introduced by the metallic reaction.

CVD SiC flexural strength

Results of the flexural strength tests are summarized in Table 1. The Weibull plots of the flexural strength are compared in Fig. 2 for unirradiated and irradiated conditions. An example of 650ºC-irradiated specimen, broken during disassembly, before machining into microbeams is shown in the inset. These pits The average strength remained practically unchanged for the case of 300ºC irradiation but decreased by ~17%

after 650ºC irradiation. The Weibull modulus (m in Fig. 2) decreased from unirradiated value of 6.6 to ~3. Reductions in Weibull modulus have been reported for neutron-irradiated CVD SiC: it decreased from the typical unirradiated values 9 - 10 to 7 – 8 in average with larger specimens.[11, 15] Compared to these results, the unirradiated Weibull modulus 6.6 appears significantly low, and the irradiated m values of ~3 appear to be very low. Moreover, Weibull moduli for flexural strength of irradiated CVD SiC tested in the exactly same way were 5.9 and 5.3 for ~2.3 dpa at 500ºC and ~4.5 dpa at 800ºC, respectively, where as those obtained through four-point-1/4 flexural test using full size specimens were 5.5 and 8.7 for ~2.0 dpa at 500ºC and ~2.0 dpa at 800ºC, respectively.[11] This indicates that the result of the present three point flexural test is likely affected by the very small specimen size and/or the associated test procedure.

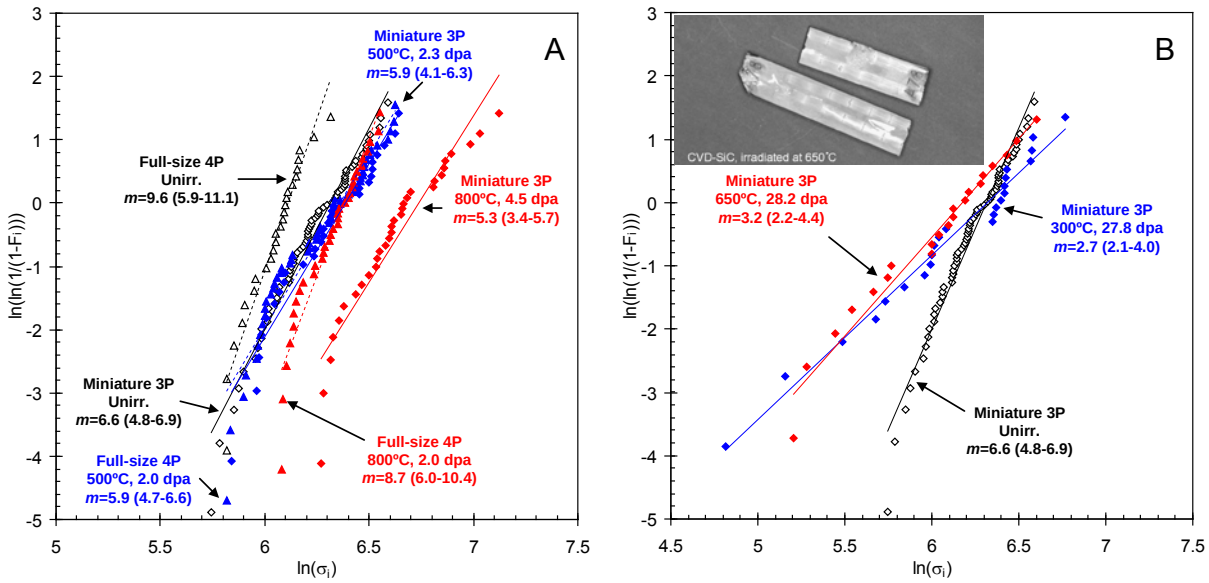

Figure 2: Weibull statistical plot of flexural strength of unirradiated and irradiated CVD SiC; A) Comparison of full-size four-point-1/4 (4P) and miniature three-point (3P) flexural configurations for unirradiated and irradiated conditions, and B) Result from miniature 3P flexural test of high dose-irradiated samples. *m* denotes Weibull shape parameter and range in parenthesis indicates 95% confidence bound for *m* value. Full-size 4P data were taken from Ref. [11] The inset photo shows appearance of sample irradiated at 650ºC in contact with stainless steel springs showing severe reaction which has lead to failure.

A closer observation of the Weibull plot reveals that presence of the low strength populations which seem to be somewhat disconnected from the higher strength populations are effectively lowering the m values for the high dose irradiated samples. This likely bi-modal strength distribution implies that the weaker populations had been affected by an additional weakening mechanism, which in this case is the reaction with the metallic springs.

Figure 3 plots the irradiated flexural strength of CVD SiC normalized to the unirradiated strength in the present and previous published work as a function of neutron fluence. The irradiation temperatures for the data points vary in a range 300 - 1300ºC. The plot indicates that the unirradiated strength of high purity CVD SiC retains its strength at least to a dose of 30 dpa, in contradiction to the precipitous decline at >10 dpa suggested by the work by Dienst.[8, 16-17] The current data further supports the suggestion of previous authors [3, 11] that the Dienst work may have been compromised by inadequate statistics, off-shoichiometric material, or mishandling of the materials during capsule disassembly, all of which were discussed by Deinst and co-authors.

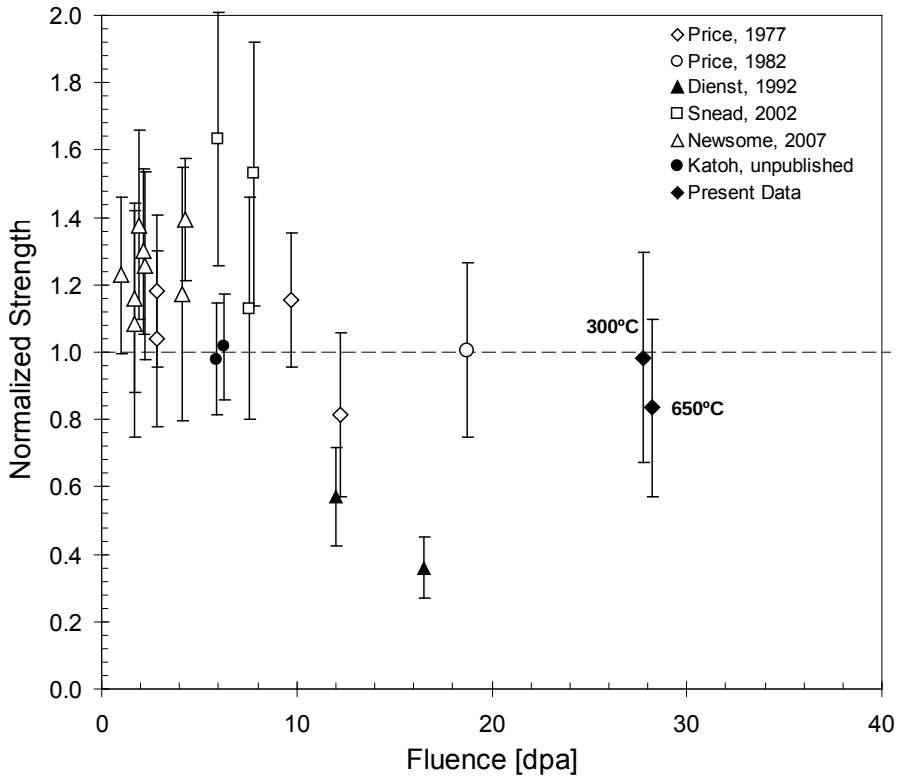

Figure 3: Strength of irradiated CVD SiC, normalized to unirradiated strength, plotted against neutron fluence. Irradiation temperatures for literature data are in a range 300-1300ºC. Error bars represent one standard deviation.

Composite flexural strength

The composite material retained its unirradiated ultimate and the proportional limit stresses after irradiation to 40.7 dpa at 800ºC, Table 1. Moreover, no significant increase in data scatter was observed for either property. Slight increases in both the ultimate and proportional limit stresses may have been the case, but this increase is not statistically significant. Examples of the recorded load – crosshead displacement curves are presented in Fig. 4, showing no noticeable difference between the unirradiated and irradiated conditions. From these observations and accepted composite theory[18] it can be reasonably concluded that no significant effect of irradiation on either the fracture energy of the matrix material, CVI SiC (essentially the same structure as the CVD material discussed herein), or the statistical strength properties of the reinforcing fibers. The fact that the matrix material retained the original strength implies that the apparent strength reduction observed for CVD SiC irradiated to a lower dose at a slightly lower temperature does not represent the neutron irradiation effect but is likely related to the reaction with the steel springs.

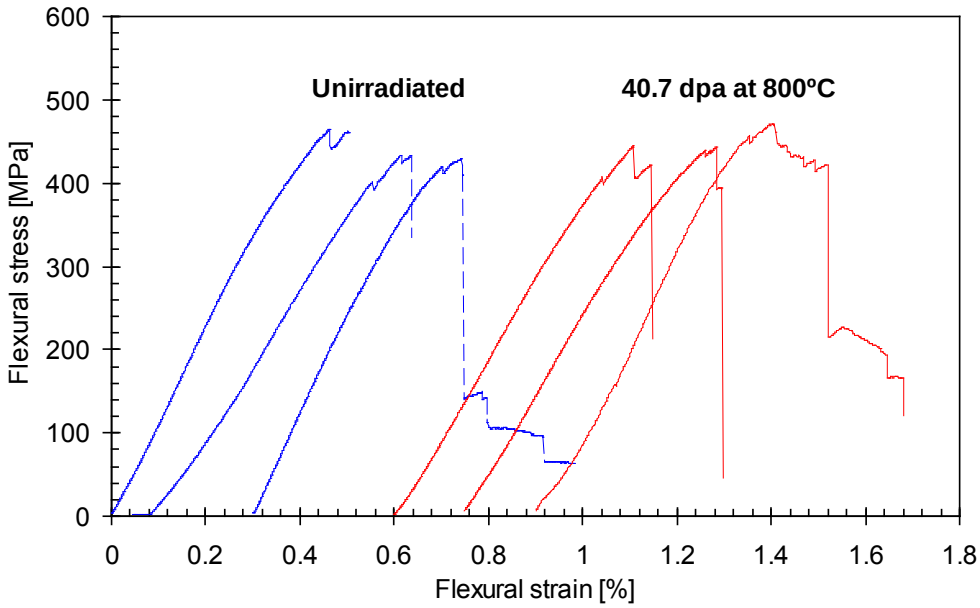

Figure 4: Examples of four-point flexural load – crosshead displacement curves for unirradiated and irradiated Hi-Nicalon™ Type S, CVI SiC matrix composites. Charts are offset for visibility purpose.

Fracture surfaces images of the broken samples are shown in Fig. 5. The higher magnification composite fracture surfaces and the fiber fracture surfaces shown are those in locations under tensile stress during testing. The composite fracture surfaces are characterized by the generally very short yet finite fiber pull-out length and the debond/slide at the interface of the fiber and the interphase whether or not the material has been irradiated. Both the unirradiated and irradiated fiber surfaces appear to be typical of the intact Hi-Nicalon™ Type-S fibers presenting river-like patterns originating from indefinite mirrors around the fracture origins either on the surface or at the fiber interior. No significant different in the fracture surfaces, irradiated and unirradiated, is observed.

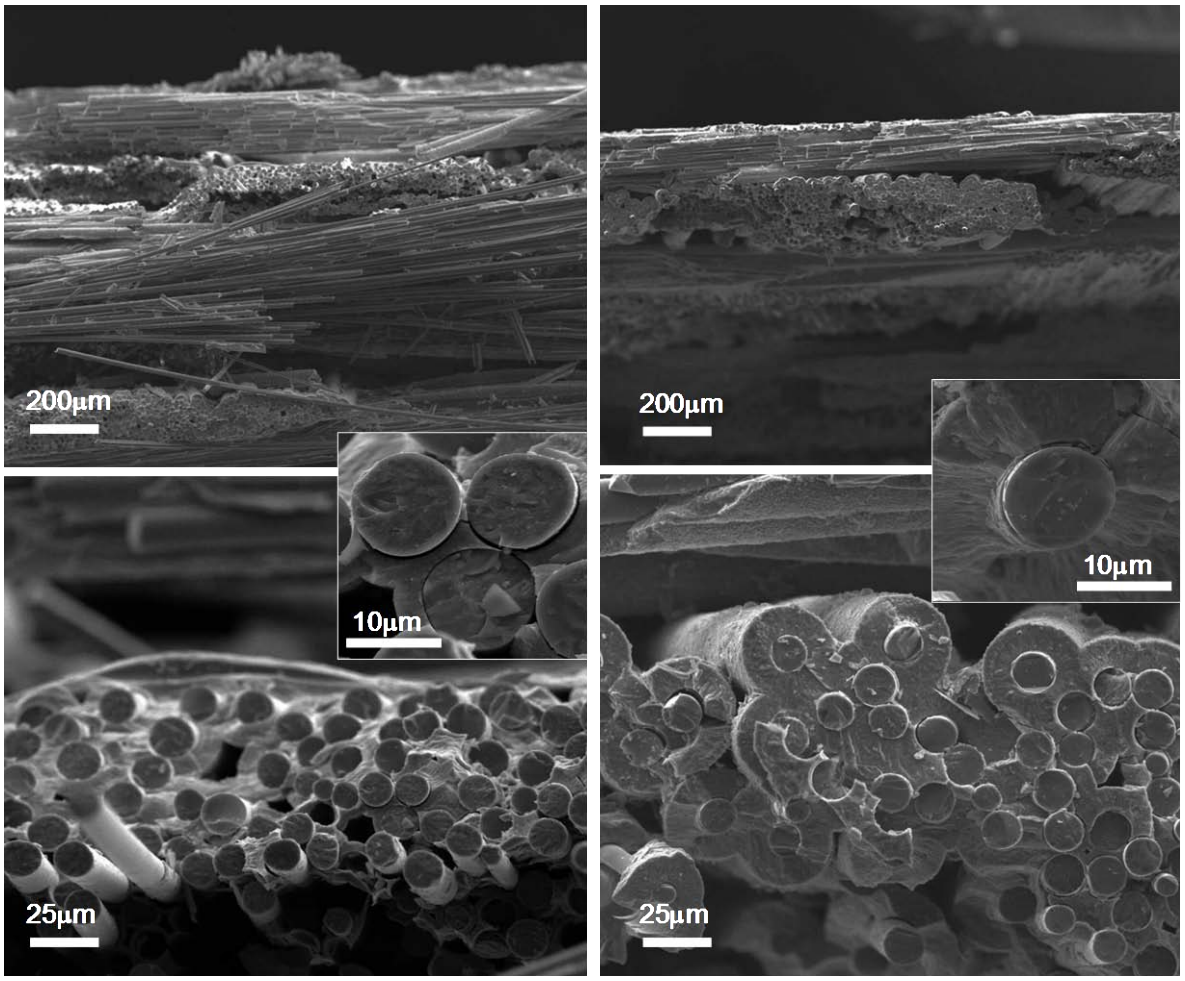

Figure 5: Scanning electron micrographs of fracture surfaces of unirradiated and irradiated Hi-Nicalon™ Type S, CVI SiC matrix composites.

Composite electrical conductivity

The direct current electrical conductivities for the in-plane (one of the fiber directions) and the through-thickness directions are plotted in Fig. 6 as a function of the measurement temperature. The temperature dependence for the unirradiated composite in both directions indicates the dominance of pyrocarbon interphase conduction, until conduction through the matrix SiC starts to contribute at ~500ºC, in a parallel circuit of pyrocarbon and SiC. The pyrocarbon is much more conductive than SiC and exhibits very weak temperature dependence, practically offering an electrical short circuit. The unirradiated in-plane conductivity 160 S/m at room temperature appears consistent with the previous works [13, 19-20] and indicates the effective conductivity ~3 x 104 S/m for pyrocarbon. The trans-thickness conductivity 5.5 S/m at room temperature indicates the effective transverse bypass efficiency ~3.4% for the pyrocarbon interphase network, again consistent with results for multilayer interphase composites in the previous work.[13]

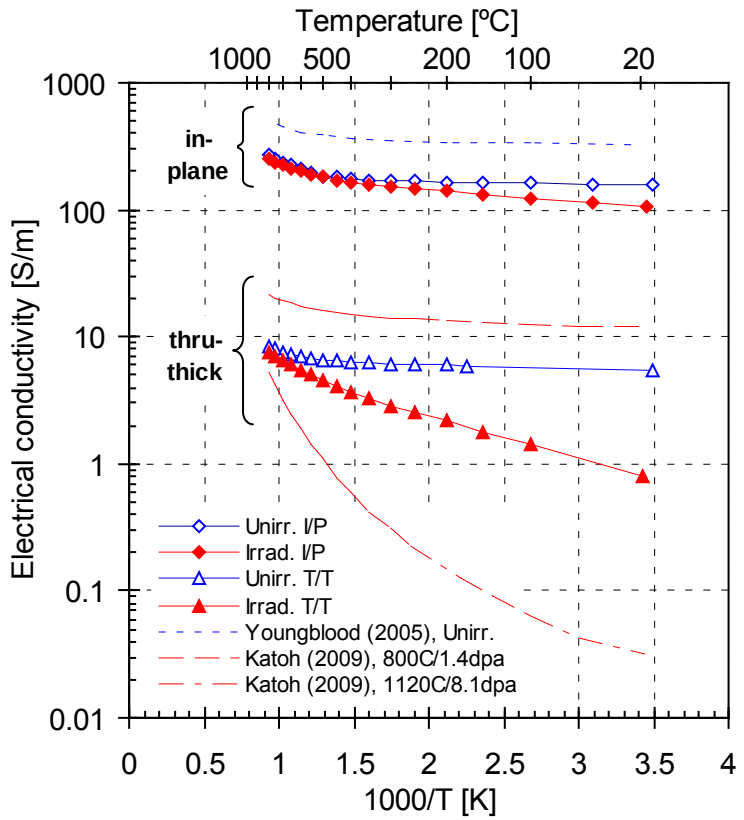

Figure 6: Electrical conductivity of unirradiated and irradiated Hi-Nicalon™ Type S, CVI SiC matrix composites.

The irradiated in-plane conductivity appears to be slightly lower than the unirradiated conductivity, to some extent consistent with the previous data after irradiation to 7.7 dpa at 800ºC.[19] The reduced in-plane conductivity at relatively low temperatures indicates the reduction in pyrocarbon conductivity to the same fraction, because the conduction is dominated by the pyrocarbon interphase. This leads to an interesting implication that the pyrocarbon conductivity, constant over a broad temperature range before irradiation, becomes temperature dependent after irradiation. The through-thickness electrical conductivity of the irradiated composite confirms the same trend with more pronounced effect of irradiation lowering the electrical conductivity at relatively low temperatures. Regardless of the orientation, the effect of irradiated on electrical conductivity at high temperatures appeared not to be very significant.

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